

# Depletion and “fines” effects on transport in hard-sphere colloids<sup>\*†</sup>

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## ABSTRACT

The effect of depletion forces induced by the presence of much smaller  $B$  spheres (diameter ratio 10/1) has been investigated in dense hard  $A$  spheres by simulation for systems of  $10^4$  spheres with mole fraction of larger spheres  $x_A = 0.05$  and with total sphere volume fraction from 0.35 to 0.655. The depletion force steeply increases in the  $A$ - $A$  pair distribution function at contact, and creates a lower first coordination and more open network  $A$ -structures. There is no evidence of demixing. It is found that in the amorphous solid region there is an enhanced diffusive mobility of the larger spheres, relative to that of pure spheres, when observed at the same densification rates. This observation resembles the “fines” effect that occurs in colloidal suspensions and granular fluids.

KEY WORDS: fines effect, depletion force, hard-sphere, computer simulation.

## 1. INTRODUCTION

Colloidal particles in equilibrium with a medium containing much smaller Brownian particles experience a thermodynamic attractive force when they approach one another at short distances [1]. This is known as the depletion force because it is due to the exclusion of the “fine”  $B$  particles from the space between the “coarse”  $A$  particles.

Binary hard-sphere fluids with a large size ratio ( $\sigma_A/\sigma_B > 5$ , where  $\sigma_A$  is the diameter of the  $A$  spheres, and  $\sigma_B$  is the diameter of the  $B$  spheres) have been of recent interest because several theories predict a region of two coexisting fluid phases [2, 3, 4, 5]. Such behavior is conceivable when the thermodynamic depletion force between the larger particles is sufficient to cause a gas-like to liquid-like condensation of component  $A$ . Stabilized colloidal dispersions, where the interactions are approximately hard sphere, have been investigated for such effects [6, 7, 8, 9]. These experiments show no indication of two coexisting fluid phases, but rather a homogeneous phase consisting primarily of small spheres mixed in with a network of large spheres in which the small spheres are still highly diffusive but the large spheres much less so. In a recent simulation study of the 10/1 ratio system [10], we found no evidence of thermodynamic demixing in the composition regions where such demixing is predicted by theory.

Although the thermodynamic properties of these binary colloids turn out to be rather unremarkable, and do not show a fluid-fluid demixing transition, there is evidence of unusual transport properties at high concentrations of large particles. The presence of the small particles enhances the mobility of the larger particles. This intriguing phenomenon, observed in mixed granular media and powders, is referred to as the “fines effect.” When a tiny amount of a fine powder is added to an immobile granular fluid or coarse powder, either in suspension or in a gas-fluidized bed, it can significantly increase the mobility of the coarse particles without changing the total volume occupied by the system.

We previously reported [10] the effects of depletion forces; these forces are induced by the presence of much smaller spheres, on the equilibrium thermodynamic properties and structure of dense hard-sphere fluids. These results, at least for the equilibrium properties, apply also, via the law of corresponding states, to the thermodynamic osmotic pressure equation-of-state and equilibrium structures of hard-sphere colloidal suspensions in equilibrium Brownian motion. The effects

are therefore amenable to experimental investigations by adding “fines,” or rheology modifiers, to hard-sphere colloidal suspensions; such experiments on sedimentation and filtration rates have been reported very recently, and they do indeed show enhanced transport rates with the addition of fines, in the form of rheology modifiers that increase the viscosity of the medium [11]. It is quite remarkable that such additives that increase the medium’s viscosity can actually increase the rates of many processes, such as sedimentation and filtration.

In our previous simulations [10], it was further found that the depletion force significantly increases the partial pressure (osmotic pressure) of the larger spheres (colloidal particle). There is a tendency of the larger (colloidal) sphere to form more open structures and, eventually, with increasing concentration, to gel into an open network with a low number coordination ( $\approx 4$  to 5). In the present paper, we report further molecular dynamics (MD) simulations designed to examine the effects of the depletion force on the transport, notably the diffusivities, of binary hard-sphere fluids in the high density range of the metastable and glassy states of the hard-sphere fluid. The motivation for the present additional study arose because inspection of the diffusivities of component  $A$  as a function of mole fraction (see Fig. 1) indicated that at higher densities, the diffusivities of spheres in the presence of fines can be greater than that of pure spheres, given that other conditions (i.e., packing fraction and compaction rate of  $A$ ), are equal.

Here we report that there is indeed a crossover. Above about  $y_A = 0.57$  volume fraction of  $A$ , the effect of adding smaller particles can be to increase the diffusivity and fluidity over dense hard spheres, even though the overall viscosity may increase. This is in contrast with the Stokes-Einstein relation that usually predicts qualitatively correct diffusion behavior. Similar “fines” phenomena are well-known to chemical engineers in the area of powder technology, but this behavior has not hitherto been observed in a model system as simple as that of binary hard sphere fluids. These and future simulations could therefore lead to a better understanding and a more formal description of the “fines” effect.

It appears that there is a connection, for systems of dense spheres, between the “depletion force” effect and the “fines” effect. One objective of the present simulations is to establish the effect, in conjunction with experimental investigations [11], and subsequently to elucidate that connection. That the effects we observe in binary spheres with a size ratio of 10/1 and the “fines” effect may be one and the same is supported by the simple observation that, even though the number

composition  $x_A = 0.05$  (i.e., 95% fines by number), the corresponding volume-percentage of fines is only of the order 1%.

## 2. MOLECULAR DYNAMICS SIMULATIONS

In order to elucidate these experimental effects, a binary hard-sphere fluid of diameter ratio 0.1 has been investigated by MD simulations. The reason for this choice is that the fine particles are sufficiently small that they can diffuse through all possible holes and cavities among the larger  $A$  particles. The triangular hole has an inscribed diameter of  $\approx 0.155\sigma_A$ , and the tetrahedral cavity has an inscribed sphere of diameter  $\approx 0.225\sigma_A$ . The size ratio of 0.1, however, is still sufficiently large to make the investigation of depletion phenomena, in the region where significant effects are predicted, accessible via Monte Carlo and MD computations using modern workstations.

The approach of the computer simulations reported here is to view the behavior of the hard-sphere fluid, both with and without the fines, to determine the effect of the addition of the small spheres to the structure and properties of the larger particles.

MD simulations were performed for binary hard-sphere systems with the masses of  $A$  and  $B$  spheres set equal to unity (in hard-sphere reduced units). In all the MD runs, periodic boundary conditions were employed, and the total number of particles in the primary box were  $N = N_A + N_B = 10^4$ , where  $N_A$  is the number of  $A$  spheres, and  $N_B$  is the number of  $B$  spheres. In the original study [10], the number of large particles ranged from 50 ( $x_A = 0.005$ ) to  $10^3$  ( $x_A = 0.1$ ). In the present extension, we report further computations in the high density range for  $N_A = 500$  ( $x_A = 0.05$ ).

In order to access the metastable high-density range, a procedure similar to that reported previously [12] was adopted for the densification of the hard-sphere fluid to produce the amorphous solid states. The density is gradually increased by isotropic compaction. It is computationally more expedient, however, to characterize the densification rate process by keeping the total volume of the system constant and acting on the equations of motions of the spheres by increasing the hard-sphere diameters uniformly as a function of time. The densification parameter that characterizes the amorphous solid (in addition to  $p\sigma^3/(k_B T)$ , where  $p$  is the system pressure,  $T$  is the system temperature, and  $k_B$  is the Boltzmann constant) is therefore  $d\sigma_A/dt$  (i.e., the reduced rate

of expansion of sphere  $A$  diameters in the compaction process). It should be noted that this is identically equivalent to an isotropic compression rate  $dV^{1/3}/dt$ , where  $V$  is the total volume of the system.

The properties of dense amorphous states of all nonequilibrium materials depend not only upon the density and temperature at which they exist, but also on the rate constant(s) of the process that produces the material in that state. To characterize an amorphous solid of hard spheres, or a binary mixture thereof, there is just one thermodynamic constant ( $p$  or  $T$ ) and one compaction rate constant  $dV^{1/3}/dt$  (or, equivalently,  $d\sigma_A/dt$ ).

In MD computations for hard spheres, one solves the quadratic equation for the time to the next collision  $t_{ij}$  between two spheres  $i$  and  $j$ , which at  $t = 0$  are separated by  $\mathbf{r}_{ij}$  and moving with relative velocity  $\mathbf{v}_{ij}$ :

$$t_{ij} = [-b_{ij} \pm (b_{ij}^2 - a_{ij}c_{ij})^{1/2}]/a_{ij}. \quad (1)$$

If at  $t = 0$  the collision diameter between species  $i$  and  $j$  is  $\sigma_{ij0}$ , then the three coefficients in Eq. (1) for the time to the next collision of expanding spheres become

$$\begin{aligned} a_{ij} &= \mathbf{v}_{ij} \cdot \mathbf{v}_{ij} - \left( \frac{d\sigma_{ij}}{dt} \right)^2 \\ b_{ij} &= \mathbf{v}_{ij} \cdot \mathbf{r}_{ij} - \sigma_{ij0} \left( \frac{d\sigma_{ij}}{dt} \right) \\ c_{ij} &= \mathbf{r}_{ij} \cdot \mathbf{r}_{ij} - \sigma_{ij0}^2. \end{aligned}$$

For the binary mixture the rate of densification is fixed by specifying  $d\sigma_A/dt$  for component  $A$ ; the corresponding rate of expansion of the fines, component  $B$ ,  $d\sigma_B/dt$ , and the cross-collision rate  $d\sigma_{AB}/dt$  are adjusted to maintain the size ratio and relative volume fractions constant.

Beyond fluid freezing, the pure hard-sphere fluid is metastable. On the other hand, the phase diagram of the hard-sphere fluid with fines is presently unknown. Recent approximate predictions using a Hamiltonian based upon an effective two-body depletion potential indicate that the presence of the “fines” extends the two-phase solid-fluid region [13]. If this were to be the stable behavior, then the present computations would also correspond to metastable states of the binary system. In both cases, however, the properties of the metastable supercooled hard-sphere fluid, with and without fines, and its glassy states depend upon the densification rate.

The partial pressures were calculated from the virial theorem, and the diffusion coefficients were calculated from transient metastable mean-square displacement time curves and averaged over time scales short compared to relaxation times.

### 3. RESULTS AND DISCUSSION

Computations were carried out for the composition  $x_A = 0.05$  in the high-density range from packing fraction  $y = 0.35$  up to close packing. The system was densified stepwise and sampled in a similar manner and at the same rate  $d\sigma_A/dt$  as reported previously for pure spheres [12]. As before, the diffusion coefficients and pressures were sampled at intermediate stages that permit some further relaxation of spheres in the compression process. The numerical results are summarized in Table I.

The binary system at the composition  $x_A = 0.05$  is stable up to around  $y = 0.5$ . Then, continuing to densify from a fully equilibrated sample at  $y = 0.5$ , at the same rate  $d\sigma_A/dt = 0.1$  as that reported in Ref. [1] the compressed metastable states were produced, sampled for the partial pressures and diffusion data, compressed to 0.55, and then compressed to 0.6, sampled again, and so on, until near close packing at  $y = 0.656$  the pressure diverges, as does also the computer cpu time! The results are given in Table I and compared with the pressure and diffusion data obtained for pure hard spheres.

Also included in Table I are some results obtained for a pure hard-sphere fluid that has been compressed at a much faster rate  $d\sigma_A/dt > 10$ . It is well known that fast quenching of spheres leads to the widely studied random-close-packed state, sometimes referred to as Bernal's glass, whereupon the pressure diverges at the random-close-packed packing-fraction density of  $y = 0.6366$ . The results do indeed show a crossover. The effect of the small spheres is to enhance the diffusivity of the otherwise immobile hard-sphere glass in the density range from approximately 0.58 to 0.64.

Figure 1 compares the diffusion data of  $A$  in the high-density range of  $x_A = 0.05$  to all the data from the previous study [10]. Diffusion coefficients for the  $A$  spheres are plotted as functions of the packing fraction of  $A$  in the mixture. The diffusivity of  $A$ ,  $D_A$  decreases as the packing fraction increases. For  $y_A$  less than 0.5, the diffusivity of  $A$  in the mixture is everywhere less than the

diffusivity of pure spheres at the same  $y_A$ . However, inspection of these data alongside the diffusion data for pure spheres shows that all the  $D_A$  data for different mole fractions, if extrapolated to higher density, head for a crossover. This would imply that, at high density, the effect of the presence of the small spheres is to increase the diffusivity of otherwise glassy states of a hard sphere solid.

The diffusion coefficient for pure hard spheres at high densities ( $y > 0.25$ ) can be represented by the Doolittle equation [12, 14], an exponential free-volume model [15],

$$D = D_0 \exp[B/(\rho - \rho_g)] \quad (2)$$

where  $D_0 = 0.3$ ,  $B = 0.75$ , and  $\rho_g$  is the glass transition density, at which  $D$  becomes zero ( $\rho_g \sigma^3 = 1.216$ ). Figure 1 also shows the data for pure hard spheres from reference [12] fitted to the Doolittle form.

It has been found that the effect of the depletion forces in the binary system is to increase the partial pressure of  $A$  above the pure hard-sphere fluid pressure. This can be explained by the depletion force causing an increase in the pair distribution at contact, which is proportional to the excess pressure over the ideal gas. At high densities, in the metastable fluid/glass region, the pressure of the system of pure spheres depends upon the rate of compaction. The greater the compaction rate the higher the pressure. Figure 2 shows the hard-sphere fluid pressures for fast and slow compactions. The present pressure data for slow compaction of the binary system show that the partial pressure of  $A$  in the high-density range is much closer to the pressure of the pure system that has been produced at the higher compaction rate and hence has not been permitted to relax to more comfortable local structures.

The reasons for the enhanced diffusivity and for pressures closer to the fast-quenched hard-sphere glass can be seen from the radial distribution functions (rdf) (Figure 3) of the respective structures near close-packing. Figure 3a shows the rdf's for the binary system in the glassy state at  $y = 0.64$ . Also superimposed on the  $A$ - $A$  rdf is the well-studied rdf that is obtained from fast random close-packing of pure hard spheres without relaxation. The similarity is quite remarkable. It appears that the influence of the fines throughout the densification process is to prohibit the local reorganization of spheres into would-be crystal nucleites or more compact, comfortable, local structures that occur in the system of pure spheres. This characteristic rdf of random close packing



is in sharp contrast to that obtained for the hard-sphere glass, in which relaxation is allowed along the metastable supercooled fluid line (Fig. 3b).

When the hard-sphere fluid is compacted slowly, relaxation processes leading to crystal-fluid heterogeneities can occur [16], but when working with small systems with as few as 500 spheres, the heterogeneous nature of the structures may not be apparent [17]. Our results suggest that one effect of the presence of fines in the metastable hard-sphere fluid is to suppress the tendency to organize to local close-packed structures, potential fcc or rhcp nucleites, which cause the sharp, non-Arrhenius, decrease in diffusivity in the pure fluid as the glass transition is approached. The evidence we have from other simulations is that the depletion force favors lower coordination bcc structures. The bcc solid was not considered in Ref. [13], so the question of the phase diagram remains open.

Finally, there is some interest in the diffusive behavior of the fines themselves. This behavior is shown in Fig. 4, alongside the data for component  $A$  and for pure spheres (from Eq. (2)). Over the entire range studied, from  $y = 0.35$  to close packing,  $D_B$  exhibits Arrhenius behavior. In addition, over this entire range, if the volume available to the  $B$  spheres  $V_{free}$  is approximated by

$$V_{free} = V - N_A(\sigma_A + \sigma_B)^3, \quad (3)$$

then the diffusivity of  $B$  is given by a low density gas form in which  $V$  is replaced by  $V_{free}$ :

$$D_B = \text{const} \times V_{free}. \quad (4)$$

## 4. CONCLUSIONS

We have found that the addition of fines to a hard-sphere fluid has an effect similar to the “fines” effect that enhances rates of transport processes in powder technology. The early indications from the structural data that we also report is that the effect of fines is to create an open structure and to impede the formation of close-packed, low diffusive, locally-ordered structures that occur when the dense metastable, pure hard-sphere fluid is permitted to relax.

A related thermodynamic “fines” effect in three-component colloidal suspensions, not previously investigated, is the enhanced Brownian motion of the colloidal particle arising from the fluctuating force due to the random fines structure. In the case of hard spheres, the fluctuations

arise from collisions with the fine particles. It is presently not clear how one resolves this effect from the depletion effect when both appear to be inextricably entangled.

Nevertheless, the effect we report for binary spheres does seem to be one and the same as seen in granular fluids and colloidal suspensions; such “fines” effects have not been previously linked to the depletion force.

## REFERENCES

- [1] S. Asakura and F. Oosawa, J. Chem. Phys. **22**: 1255 (1954).
- [2] T. Biben and J.-P. Hansen, Phys. Rev. Lett. **66**: 2215 (1991).
- [3] Y. Rosenfeld, Phys. Rev. Lett. **72**: 3831 (1994).
- [4] Y. Rosenfeld, J. Chem. Phys. **99**: 2857 (1995).
- [5] T. Coussaert and M. Baus, Phys. Rev. Lett. **80**: 4832 (1998); errata **80**: 4832 (1998).
- [6] P. D. Kaplan, J. L. Rouke, A. G. Yodh, and D. J. Pine, Phys. Rev. Lett. **72**: 582 (1994).
- [7] A. D. Dinsmore, A. G. Yodh, and D. J. Pine, Phys. Rev. E **52**: 4045 (1995).
- [8] U. Steiner, A. Meller, and J. Stavans, Phys. Rev. Lett. **74**: 4750 (1995).
- [9] A. Imhof and J. K. G. Dhont, Phys. Rev. Lett. **75**: 1662 (1995).
- [10] L. Lue and L. V. Woodcock, Mol. Phys. **96**: 1435 (1999).
- [11] R. Savage, Ph.D. thesis, University of Bradford, 1999.
- [12] L. V. Woodcock, Ann. NY Acad. Sci. **371**: 274 (1981).
- [13] M. Dijkstra, R. van Roij, and R. Evans, Phys. Rev. Lett. **81**: 2268 (1998).
- [14] A. K. Doolittle, Appl. Phys. **22**: 1471 (1951).
- [15] M. H. Cohen and D. Turnbull, J. Chem. Phys. **31**: 1164 (1959).
- [16] K. Kendall, C. Stainton, F. van Swol, and L. V. Woodcock, paper to be presented at 14th Symposium on Thermophysical Properties, June 2000 Boulder, CO.
- [17] S. Torquato, T. M. Truskett, and P. G. Debenedetti, Phys. Rev. Lett. **84**: 2064 (2000).

Table I: MD data for pressure and diffusivity of binary hard-sphere fluid compared to pure spheres

			— data for hard spheres with “fines” —				— data for pure spheres —			
$y$	$y_A$	$\rho_A$	$p_{AA}$	$p_{AB}$	$p_{BB}$	$10^3 D_A$	$10^3 D_B$	$p_{fast}$	$p_{slow}$	$10^3 D$
0.350	0.3435	0.6560	3.74	10.26	13.01	18.85	347.1	3.294	3.307	129.51
0.400	0.3925	0.7497	5.78	15.02	15.04	12.71	269.6	4.971	4.989	82.81
0.450	0.4416	0.8434	9.11	21.56	17.14	7.463	206.1	7.511	7.552	49.52
0.500	0.4907	0.9371	14.35	30.68	19.37	3.688	156.4	11.443	11.468	23.21
0.550	0.5397	1.0308	24.13	43.06	21.77	1.401	118.9	17.697	17.731	4.86
0.600	0.5888	1.1246	42.86	60.71	24.41	0.361	84.4	41.569	29.866	0.05
0.620	0.6084	1.1620	61.84	68.95	25.57	0.153	71.9	75.322	35.463	0
0.630	0.6183	1.1808	81.19	73.01	26.20	0.078	65.9	119.371	42.658	0
0.640	0.6281	1.1995	123.76	76.99	26.82	0.037	60.4	264.861	54.954	0
0.650	0.6379	1.2183	281.43	81.07	27.46	0.005	55.2	>10000	75.858	0
0.655	0.6428	1.2276	1033.01	83.03	27.79	0.001	55.1		97.724	0
	0.6640	1.2682							724.436	

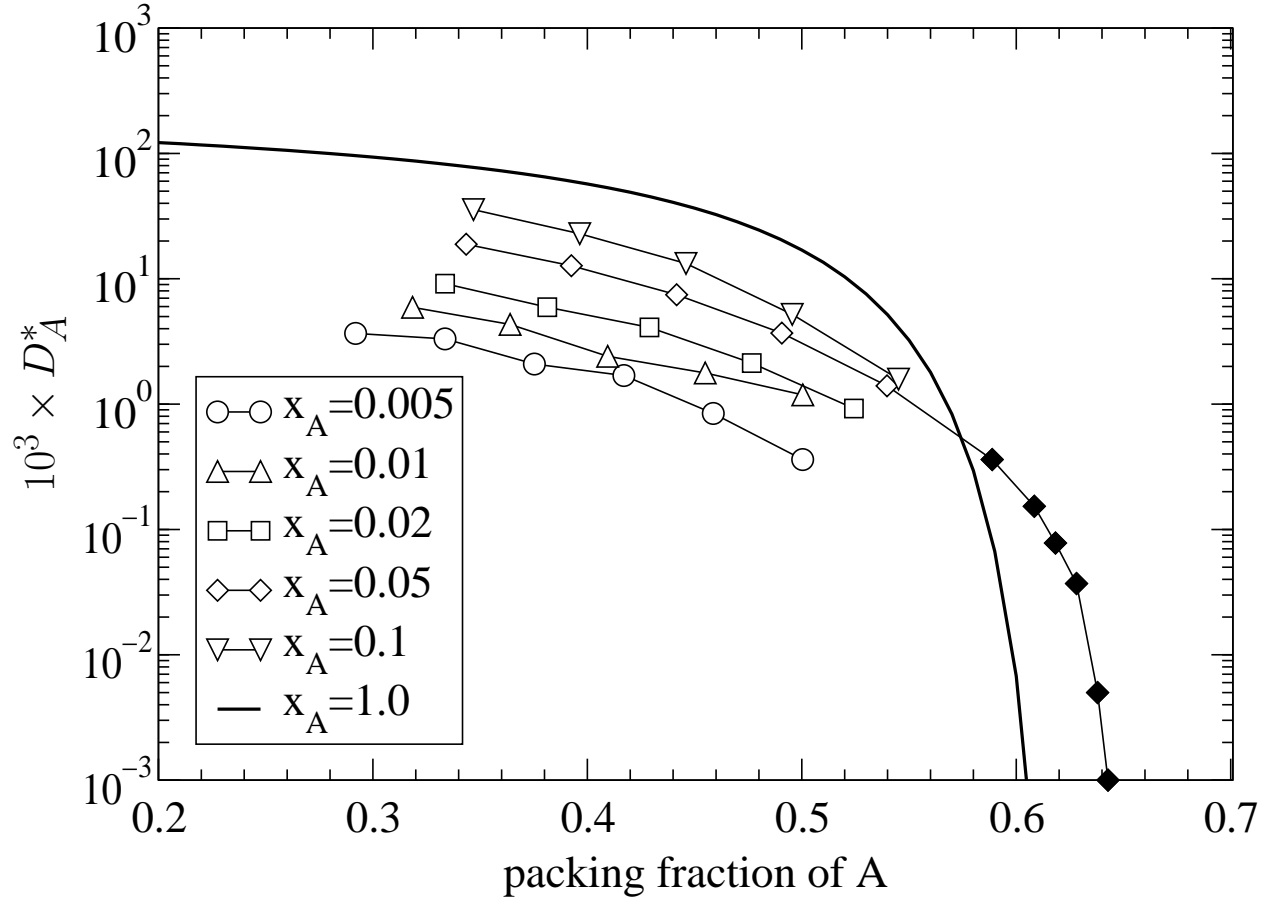


Fig. 1: Diffusivity of hard sphere fluids as a function of the packing fraction of  $A$ . The solid line is the diffusion coefficient data for pure hard spheres, represented by Eq. (2) and taken from reference [12]. The open circles, triangles-up, squares, diamonds, and triangles-down correspond to the mole fractions  $x_A = 0.005, 0.01, 0.02, 0.05$ , and  $0.1$ , respectively, and are taken from Ref. [10]. The new data (solid diamonds) show the crossover effect at the mole fraction  $x_A = 0.05$ .

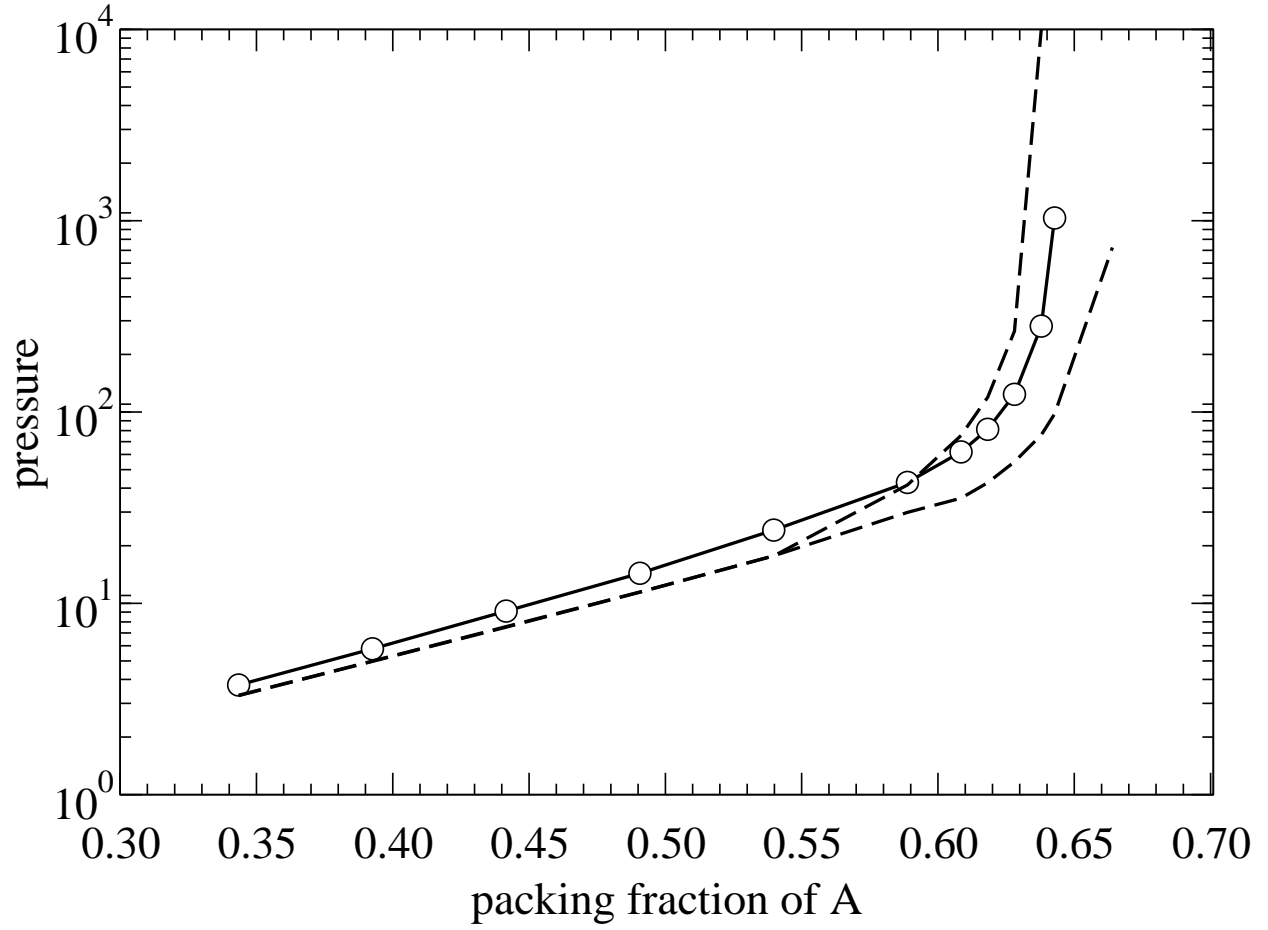


Fig. 2: Partial pressures of component  $A$  spheres (circles) compared with the hard-sphere pressure data for pure spheres (dashed-lines) taken from the equation-of-state data from Ref. [12].

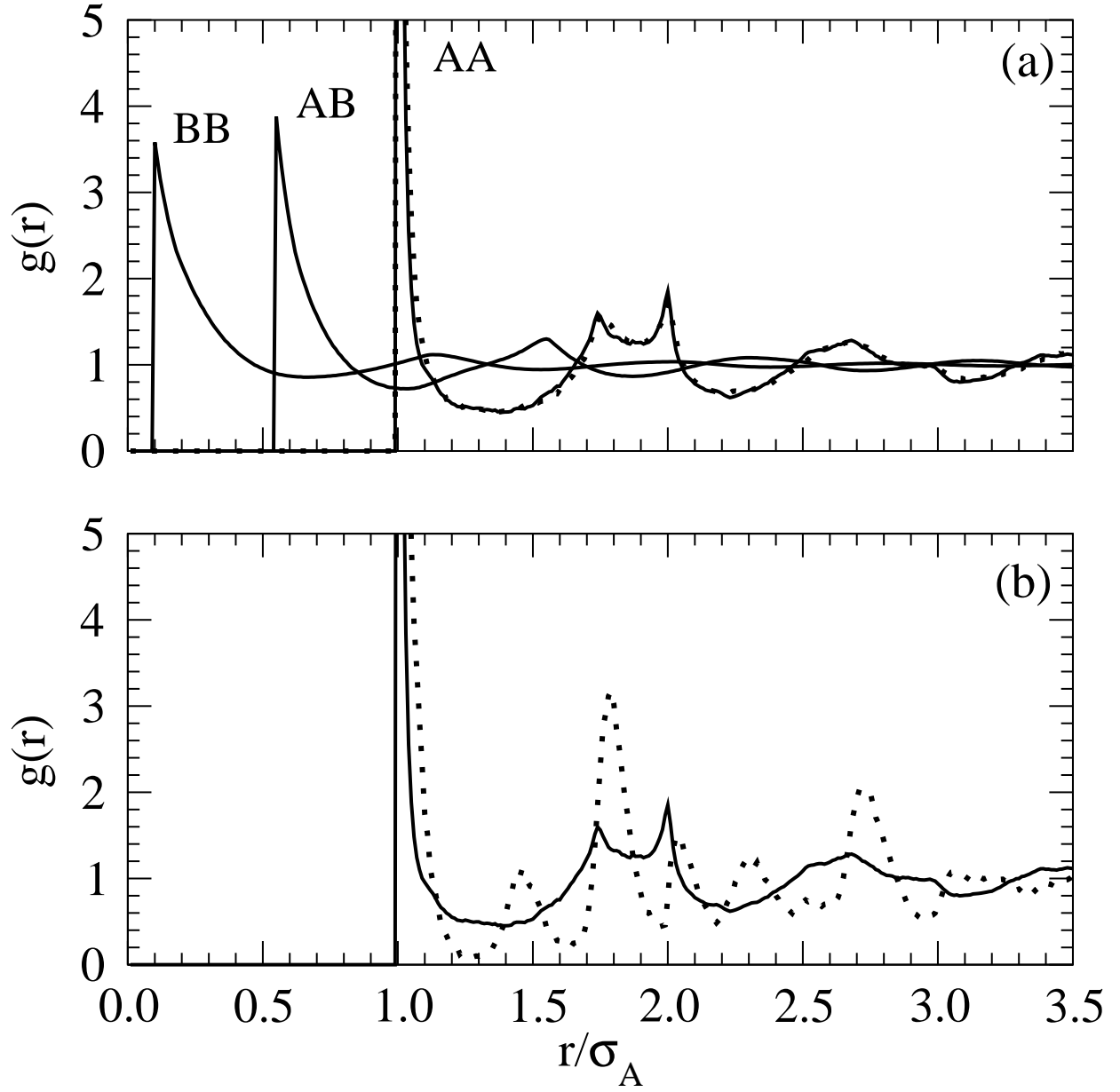


Fig. 3: a. Radial distribution functions of the binary system  $x_A = 0.05$  at the density  $y_A = 0.64$  (solid lines) produced at the densification rate  $d\sigma_A/dt = 0.1$  compared to one-component hard-spheres in a glassy state at the (fast) random close-packed state (dotted line). b. Radial distribution function for A-A pairs (solid line) compared to the RDF obtained for pure spheres (dotted line) when pure spheres are compacted at a similar densification rate.

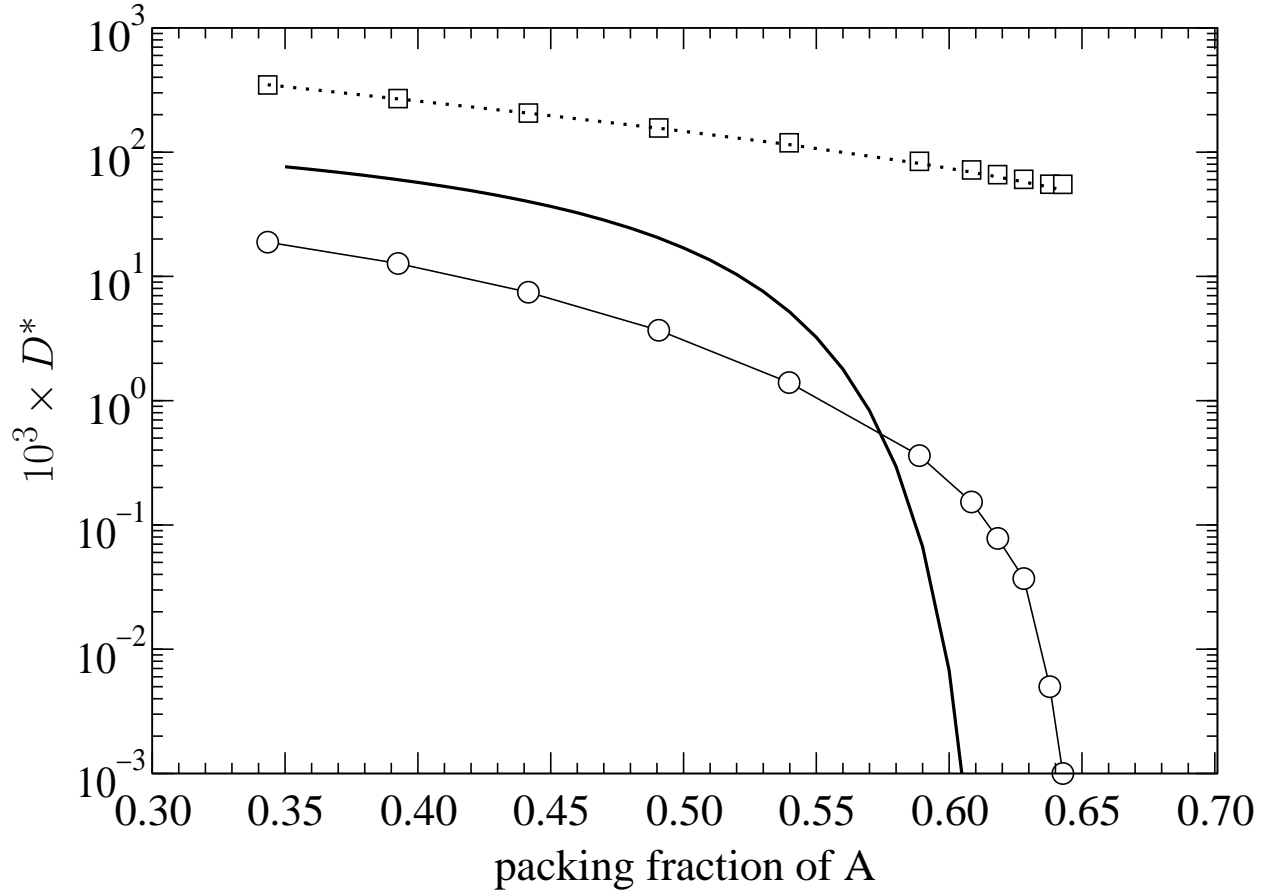


Fig. 4: Diffusion data for  $B$  spheres (squares) showing mobility and Arrhenius behavior compared to the non-Arrhenius behavior of the  $A$  spheres, both with (circles) and without (solid line) the fines. The dotted line is the diffusion of  $B$  using a simple free-volume approximation. For the size ratio 0.1, the small spheres retain a high diffusivity right up to close packing of  $A$ .